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COMPLETE SPECIFICATION

Fluorocarbon Acid and Derivatives

We, MINNESOTA MINING AND MANUFACTURING COMPANY, of 900, Bush Avenue, Saint Paul 6, Minnesota, United States of America, a corporation organised under the laws of the State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a dicarboxylic fluorocarbon acid and related di-derivative carboxylic compounds (acid halides, metal and ammonium salts, and alkyl esters).

This acid may be termed perfluorooxydipropionic acid and has the formula:—

$$HOOC—CF_2CF_2—O—CF_2CF_2—COOH$$

which can be abbreviated as:—

$$O(CF_2CF_2COOH)_2$$

The "perfluoro" prefix signifies that all carbon-bonded hydrogen atoms of the corresponding oxydipropionic acid of conventional organic chemistry have been replaced by fluorine atoms.

This acid, and the corresponding di-derivatives wherein both hydroxyl groups have been replaced to form a corresponding acid halide, metal or ammonium salt, or alkyl ester, constitute the class of novel fluorocarbon carboxylic compounds claimed herein. These derivative compounds readily hydrolyze to form the acid compound.

It has been discovered that these compounds are highly stable, the intermediate oxygen atom providing a strong linkage between the pair of fluorocarbon groups and in combination therewith providing a stable chain linking together the terminal carbonyl carbon atoms. This perfluorinated chain is highly inert and does not possess the "ether" characteristics of the oxygen-containing hydrocarbon chain of the corresponding non-fluorinated compounds of conventional organic chemistry. The present acid is much stronger than the corresponding non-fluorinated acid.

The intermediate oxygen atom permits rotation and flexibility of the fluorocarbon chain, and it lowers the refractive index. The present acid differs materially from perfluoroadipic acid, $(CF_2)_4(COOH)_2$, even though both dicarboxylic acids contain four perfluorinated carbon atoms in the linking chain.

The present acid has general utility as a dicarboxylic fluorocarbon acid in the six carbon atom range and the various derivatives have corresponding utility when use thereof is indicated in place of the acid.

This perfluoro-oxydipropionic acid has notable utility as a starting compound for making omega-hydroperfluoroethoxypropionic acid.

$$HCF_2CF_2OCF_2CF_2COOH$$

which is a new and useful highly-fluorinated monocarboxylic acid. The latter can be made in good yields by monodecarboxylation of the present acid, which can readily be effected by heating the acid with an organic base such as piperidine. So far as is known, monodecarboxylation of the present acid provides the only practical route to the preparation of this particular monocarboxylic acid and it thus provides a starting compound of unique utility for this purpose.

It has now been discovered that perfluoro-oxydipropionic acid can be made in good yields from organic starting material by electrolyzing a mixture of an oxydipropionyl halide and liquid hydrogen fluoride in a nickel-anode cell to obtain perfluoro-oxydipropionyl fluoride:—

$$O(CF_2CF_2COF)_2$$

and hydrolyzing the latter to form the corresponding acid. The electrofluorination procedure is described in the specification of our Patent No. 735,730.

This acid is a strong salt-forming acid and can readily be reacted with metal oxides, carbonates or hydroxides, or with ammonium

hydroxide, in water or in an inert reaction medium, to yield the corresponding salts. Salts can also be formed directly by reaction of a base with the perfluoro-oxydipropionyl fluoride cell product. For example, reaction of the latter with KOH yields the potassium salt, which if desired can be hydrolyzed to the acid as by mixing with concentrated sulphuric acid and distilling off the perfluoro-oxydipropionyl acid product.

The acid can be reacted with phosphorous pentachloride or phthalyl dichloride to produce the corresponding acid chloride which can be used for making the corresponding acid bromide or iodide by replacement of the chlorine with bromine or iodine, as by reacting with calcium bromide or iodide, respectively. These acid chlorides, bromides and iodides have the formulae:—

$$O(CF_2CF_2COCl)_2$$
$$O(CF_2CF_2COBr)_2$$
$$O(CF_2CF_2COI)_2$$

The acid chloride compound readily reacts with alcohols to form the corresponding esters (primary, secondary and tertiary) which contain the alkyl group of the alcohol. The acid can be reacted with primary alcohols to yield the primary esters. These esters have the formula:—

$$O(CF_2CF_2COOR)_2$$

EXPERIMENTAL EXAMPLES

A 50 ampere iron cathode nickel anode laboratory cell of the type described in the specification of our British Patent No. 686,678, was employed for electrochemical fluorination. The cell was charged with 2,000 grams of anhydrous hydrogen fluoride and with approximately 200 grams of oxydipropionyl fluoride as organic starting compound:—

$$O(CH_2CH_2COF)_2$$

The latter had been prepared by reacting with anhydrous hydrogen fluoride the corresponding oxydipropionyl chloride, which had been prepared by hydrolysis of the corresponding oxydipropionitrile compound with concentrated hydrochloric acid. The organic charge included 5% of acetic anhydride as a conductivity additive (current carrier). The cell was operated at an average temperature of 25° C. and pressure of 25 pounds per square inch (gauge). The average voltage was 5 to 6 volts and the average current density was 20 amperes per square foot of anode area. Additions of organic charge and of hydrogen fluoride were made from time to time as make-up. The crude product fraction boiling at above minus 20° C. was recovered and found to include the desired perfluoro-oxydipropionyl fluoride product compound:—

$$O(CF_2CF_2COF)_2$$

The crude cell product was added slowly to an aqueous slurry of excess calcium oxide. Filtration of the resulting solid calcium fluoride and evaporation of the filtrate produced the crude calcium salt of the desired acid. Acidification of 393 grams thereof with concentrated sulphuric acid, followed by fractional distillation, yielded 163 grams of perfluoro-oxydipropionic acid:—

$$O(CF_2CF_2COOH)_2$$

An alternative procedure involved initial recovery of perfluoro-oxydipropionyl fluoride (boiling point 60 to 70° C.) by fractional distillation of the aforesaid crude cell product. To a solution of 16 grams of sodium hydroxide and 200 milliliters of water was slowly added 31 grams of this fluoride compound. The mixture was stirred for two hours. The clear solution was then treated with 11.9 grams of calcium chloride in 50 milliliters of water, which caused a precipitate of calcium fluoride to form. After standing in a low-temperature refrigerator for two days, followed by digestion on a steam bath, the precipitate has coagulated enough to permit filtration. The filtrate was evaporated to dryness to yield 44.8 grams of a white solid, identified as the sodium salt:—

$$O(CF_2CF_2COONa)_2$$

This salt was triturated with approximately 200 grams of concentrated sulphuric acid. The mixture was poured into 300 milliliters of water and the resulting solution was continuously extracted with ether for 24 hours. The ether extract was separated, dried over anhydrous sodium sulphate and the ether removed by distillation, leaving a residue of 17.97 grams of solid material having a vacuum boiling point of 104 to 106° C. at 2 milliliters pressure. This product was identified as the desired perfluoro-oxydipropionic acid. Analysis showed 49.3% fluorine (49.7% calculated) and 23.4% carbon (23.5% calculated). The neutral equivalent value was 152, in close agreement with the calculated value of 153. This acid readily forms a hydrate in contact with atmospheric moisture which melts below room temperature.

The silver salt was prepared by reacting an equimolar mixture of silver oxide and acid in 500 milliliters of water per mole of acid. The mixture was heated on a steam bath for 45 minutes, filtered, and cooled to cause crystallization of the silver salt, which was separated by filtration and dried. Analysis showed 41.4% silver (calculated 41.5%), consistent with the formula:—

$$O(CF_2CF_2COOAg)_2$$

Reaction of the silver salt with iodine to produce the diiodide derivative by replacement of the carboxylate groups was readily accomplished. For instance, 0.10 mol of the silver salt was mixed with 0.26 mol of iodine and the mixture heated to a final pot temperature of 190° C. The crude distillate was washed with 5% aqueous KOH solution to remove free iodine and then dried over anhydrous calcium sulphate and distilled, yielding a product boiling at 137° C. (at 740 millimeters) which was identified as:—

$O(CF_2CF_2I)_2$

This compound is a colourless liquid at room temperature, having a refractive index of 1.395 at 25° C. Analysis showed 54.0% iodine (54.0% calculated).

The mercury salt obtained by reacting approximately equimolar quantities of mercuric oxide and acid, was recovered as a dry crystalline solid. Analysis showed 36.9% mercury (39.7% calculated), consistent with the formula:—

$O(CF_2CF_2COO)_2Hg$

The ethyl ester was prepared from a mixture of 214.2 grams of the acid, 137 grams of ethanol and 260 grams of benzene, which was heated in an apparatus equipped to remove the water-ethanol-benzene azeotrope which formed as esterification proceeded. After removal of the azeotrope, distillation was continued to isolate the ester product, which had a vacuum boiling point of 75° C. at 3.5 millimeters and which was identified as ethyl perfluoro-oxydipropionate, having the formula:—

$O(CF_2CF_2COOC_2H_5)_2$

The methyl ester was prepared by an alternative procedure from the sodium salt, made by neutralizing 26 grams of the acid with 6.8 grams of sodium hydroxide. This sodium salt was mixed with an equivalent amount of methyl *p*-toluene sulphonate. Reaction occurred upon heating this mixture to 230° C. in a distillation apparatus. The methyl perfluoro-oxydipropionate ester was collected, having a boiling point of 179° C. (at 740 millimeters). It was a colourless liquid having a refractive index of 1.3436 at 25° C.

Monodecarboxylation of the acid was readily accomplished by heating in admixture with piperidine. For instance, 100 grams of the perfluoro-oxydipropionic acid (0.326 mol) and 2.77 grams of piperidine (0.326 mol) were mixed in a 150 milliliter pot and heated in a Woods Metal bath. The pot was heated to a maximum temperature of 280° C. and 79.3 grams of distillate was collected to a maximum temperature of 180° C. This distillate was fractionally distilled to yield 60.0 grams of product identified as omega-hydro-perfluro-ethoxypropionic acid:—

$HCF_2CF_2OCF_2CF_2COOH$

This acid is a colourless liquid at room temperature, having a refractive index of 1.31 and a boiling point of about 155° C. (at 740 millimeters).

WHAT WE CLAIM IS:—

Perfluoro-oxydipropionic acid having the formula:—

$O(CF_2CF_2COOH)_2$

and the corresponding di-derivative acid halides, metal and ammonium salts, and alkyl esters thereof.

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